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Ground-based PM_{2.5} samples collected in Pearl River Delta (PRD) region during winter and summer (from 14 December 2006 to 28 January 2007 in winter and from 4 July 2007 to 9 August 2007 in summer) were analyzed for 30 water-soluble organic species, including dicarboxylic acids, ketocarboxylic acids and dicarbonyls, nine fatty acids, and benzoic acid. Molecular distributions of dicarboxylic acids demonstrated that oxalic acid (C₂) was the most abundant species followed by phthalic acid (Ph) in PRD region. The concentrations of total dicarboxylic acids ranged from 99 to 1340 ng m⁻³, with an average of 438 ± 267 ng m⁻³ in PRD. The concentrations of total ketocarboxylic acids ranged from 0.6 to 207 ng m⁻³ (43 ± 48 ng m⁻³ on average) while the concentrations of total α-dicarbonyls, including glyoxal and methylglyoxal, ranged from 0.2 to 89 ng m⁻³, with an average of 11 ± 18 ng m⁻³ in PRD. The total quantified water-soluble organic carbon (TQWOC) accounted for 3.4 ± 2.2% of OC and 14.3 ± 10.3% of water-soluble OC (WSOC). Hexadecanoic acid (C_{16:0}), octadecanoic acid (C_{18:0}) and oleic acid (C_{18:1}) are the three most abundant fatty acids in PRD. The distributions of fatty acids are characterized by a strong even carbon number predominance with a maximum (C_{max}) at hexadecanoic acid (C_{16:0}). Ratio of C_{18:1} to C_{18:0} acts as an indicator for aerosol aging. In PRD, an average of C_{18:1}/C_{18:0} ratio was 0.53 ± 0.39, suggesting an enhanced photochemical degradation of unsaturated fatty acid. Seasonal variations of the pollutant concentrations were found in the four sampling cities. Higher concentrations of TQWOC were observed in winter (544 ng m⁻³) than in summer (318 ng m⁻³). However, the abundances of TQWOC in OC mass were higher in summer (1.8–12.4%, 5.4% on average) than in winter (1.1–5.7, 2.6% on average), being consistent with enhanced secondary production of dicarboxylic acids in warmer weather. Spatial variations of water-soluble dicarboxylic acids were characterized by higher concentrations in Hong Kong and lower concentrations Guangzhou (GZ)/Zhaoqing (ZQ) during winter whereas highest concentrations were observed in GZ/ZQ during summer. These spatial and seasonal distributions are consistent with photochemical production and the subsequent accumulation under different meteorological conditions.

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1 Introduction

The Pearl River Delta (PRD) region in China covers nine prefectures of the province of Guangdong, namely Guangzhou, Shenzhen, Zhuhai, Dongguan, Zhongshan, Foshan, Huizhou, Jiangmen, Zhaoqing, the Hong Kong Special Administrative Region (HK-SAR), and the Macau Special Administrative Region. It has a population approximately of 40 million people. The climate of PRD is dominated by the Asian monsoon, with north wind as prevailing wind in winter and south wind in summer. PRD is one of the rapideconomic growth regions in China. As influenced by urbanization and industrialization, air pollution has been becoming more and more severe in PRD, which is one of the four heaviest haze regions in China, together with the Yangtze River Delta, Beijing-Tianjin-Tangshan and Chongqing. Particulate matter with diameter less than 2.5 micrometers ($PM_{2.5}$) has recently received much attention (Yang et al., 2005; Feng et al., 2007; Li et al., 2008). These fine particles can penetrate deeply into human's lung, and also affect visibility, environment, and radiative forcing (Penner and Novakov, 1996; Menon et al., 2002; Wilkening et al., 2000; Nel, 2005). Adverse health, environment, and climate effects of the fine particles are constitutionally derived from their chemical components and properties.

Organic acids including monocarboxylic acids, dicarboxylic acids and aromatic acids in atmospheric aerosols have been studied owing to their potential roles in affecting the global climate. These acids can reduce the surface tension of particles to form cloud condensation nuclei (Facchini et al., 1999; Kerminen et al., 2000) and are involved in a series of atmospheric chemical reactions occurring in the gas, water and particle phases (Chebbi et al., 1996; Saxena et al., 1996). Dicarboxylic acids are important components of atmospheric aerosols. Due to the hygroscopic property, they play a role in the global radiative balance (Saxena et al., 1995; Facchini et al., 1999; Kerminen, 2001). Distributions and concentrations of the organic acids in aerosols are important to understand their photochemical reactions and long-range transport. These species are emitted to the atmosphere directly from natural and anthropogenic primary sources

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(Kawamura and Kaplan, 1987; Rogge et al., 1991, 1993a; Fang et al., 1999; Schauer et al., 1999; Simoneit et al., 2002). They are also produced by secondary atmospheric chemical reactions. Total dicarboxylic acids account for ~1–3% of the total particulate carbon in urban areas and >10% in remote marine environments (Kawamura and Ikushima, 1993; Kawamura et al., 1996a, b; Kawamura and Sakaguchi, 1999; Kerminen et al., 2000).

Fatty acids were one of the most abundant compound classes in the polar organic fraction of aerosols from urban atmospheres (Oliveira et al., 2007). They were found to contribute 6–53% of identified organic compounds from emission sources such as biomass burning (Rogge et al., 1998; Nolte et al., 2001; Schauer et al., 2001; Fine et al., 2002), cooking (Schauer et al., 1999, 2002; Rogge et al., 1991; He et al., 2004), paved road dust (Nolte et al., 2002) and automobiles (Rogge et al., 1993a; He et al., 2006). Benzoic acid is a secondary product from photochemical degradation of aromatic hydrocarbons emitted by automobiles (Suh et al., 2003). This acid has also been measured as primary pollutant in the exhaust of motor vehicles (Kawamura et al., 1985; Rogge et al., 1993b).

Previous studies have quantified the organic acids in Guangzhou (Feng et al., 2006; Wang et al., 2006). However, the seasonal and spatial variations of organic acids were not studied (e.g., Feng et al., 2006). To better understand the organic compositions in the PRD region, PM_{2.5} samples were acquired at four sampling sites simultaneously during winter and summer. The main objectives of this study are to determine the spatial and seasonal variations of selected organic species and to explore their implications for sources and photochemical reactions.

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2 Experiment

2.1 Sample collection

Four sampling sites were selected in PRD region, including Sun yat-sen University in Guangzhou (GZ), Zhaoqing University in Zhaoqing (ZQ) in Mainland of China, as well as The Hong Kong Polytechnic University (PU) and Hok Tsui (HT) in Hong Kong. Their locations are shown in Figure 1. These four sites represent different types (urban: GZ; semi-rural: ZQ; urban/roadside: PU; rural: HT). Twenty-four-hour sampling of PM_{2.5} were conducted simultaneously in the four sites from 14 December 2006 to 28 January 2007 in winter and from 4 July 2007 to 9 August 2007 in summer. Fifteen samples were collected at each site for consequence organic analyses. The PM_{2.5} were acquired on pre-heated (800 °C, 3 h) quartz fiber filters (102 mm) by medium volume samplers at a flow rate of 113 L min⁻¹. The sampling flow rates were checked before and after sampling with a TSI mass flow meter (model 4040, Shoreview, MN, USA). After sampling, aerosol loaded filters were stored in a refrigerator at 4 °C to prevent loss of any volatile components. However, this temperature does not totally prevent the loss of very volatile components and does not avoid some microbial processing. Approximately 5% of field blanks were collected to subtract positive artifacts that resulted from passive adsorption of gas-phase organic compounds onto the filter during and/or after sampling. Meteorological data (from Hong Kong Observatory and China Meteorological Administration) shows that the southern air mass flow was dominated during summer, therefore GZ and ZQ were the downwind sampling locations in summer; but northern air mass flow was dominated during winter, then PU and HT were the downwind sites in winter. Molecular compositions of low molecular weight diacids (C₂–C₁₂), ketoacids (ω C₂– ω C₉, pyruvic acid), α -dicarbonyls (C₂–C₃), benzoic acid and fatty acids (C₁₂–C₂₅) were determined by gas chromatography/mass spectrometry (GC/MS). Samples were also analyzed for organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC).

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2.2 OC, EC and WSOC analysis

OC and EC were measured on a 0.526 cm^2 punch from each filter by thermal optical reflectance (TOR) following the IMPROVE protocol on a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) (Chow et al., 2004, 2005; Cao et al., 2003). This produced four OC fractions [OC1, OC2, OC3, and OC4 at 120°C , 250°C , 450°C , and 550°C , respectively, in a helium (He) atmosphere], a pyrolyzed carbon fraction [OP, determined when reflected laser light attained its original intensity after oxygen (O_2) was added to the combustion atmosphere], and three EC fractions (EC1, EC2, and EC3 at 550°C , 700°C , and 800°C , respectively, in a 2% O_2 /98% He atmosphere). IMPROVE OC is operationally defined as $\text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OP}$, whereas EC is defined as $\text{EC1} + \text{EC2} + \text{EC3} - \text{OP}$. The minimum detection limit for the carbon analysis is 0.8 and $0.4 \mu\text{gC cm}^{-2}$ for OC and EC, respectively, with a precision better than 10% for total carbon (TC).

For determination of WSOC, five punches (a total area of 2.63 cm^2) were taken from each filter and placed into a 15 ml screw-capped vial to which 5 ml of distilled de-ionized water (DDW) was added. Samples were extracted in a ultra-sonic water bath for 1 h. Filter debris and suspending insoluble particles were removed from the water extracts using a syringe filter ($0.2 \mu\text{m}$ PTFE membrane). Each filtered extract was then transferred into a clean auto-sampler fitted vial. The filtered extract was analyzed for total organic carbon (TOC) using a Shimadzu TOC-V CPH high-sensitivity Total Carbon Analyzer (Columbia, MD, USA). The minimum detection limit is $15 \mu\text{g L}^{-1}$, with a precision of $\pm 5\%$. Negligible amounts of OC, EC, and WSOC were observed in the field blanks. The data reported here are all corrected for the blanks.

2.3 Inorganic compounds analysis

Inorganic ions were determined using an ion chromatograph (IC) gradient pump (LC40) with a conductivity detector (CD25) (Dionex, Sunnyvale, CA, USA). An analytical column (AS11, 4 mm) with a guard column (AG11, 4 mm) and an anion trap column was used for inorganic anion detection with gradient elution from 0.2 to 5 mM NaOH. A

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cation analytical column (CS12, 4 mm) with a guard column (CG12, 4 mm) was used to analyze inorganic cations with an eluent of 20 mM methanesulfonic acid.

2.4 Organic acid analysis

The details of sample extraction and derivatization were documented elsewhere (Kawamura 1993; Kawamura and Yasui, 2005; Ho et al., 2010). An aliquot of the sample was extracted with pure water (10 ml \times 3) to isolate low molecular weight dicarboxylic acids, ketoacids and α -dicarbonyls as well as free fatty acids. After concentration, the extracts were reacted with 14% BF_3/n -butanol at 100 °C to convert the carboxyl groups to butyl esters and the aldehyde groups to dibutoxy acetals. The derivatized total extracts were analyzed with a Hewlett-Packard 6890 GC installed with HP5 fused silica capillary column (25 m \times 0.20 mm i.d., 0.5 μm film thickness) and flame ionization detector. Authentic standards were used for the peak identification based on GC retention times. Homologous series of fatty acids were determined as butyl esters (Mochida et al., 2007). Mass spectral confirmation of the compounds was achieved using ThermoQuest Trace GC/MS (Austin, TX, USA) using a similar GC conditions. Recoveries of the dicarboxylic acids, ketocarboxylic acids, α -dicarbonyls, and fatty acids were $>70\%$. The reproducibility errors of the methods for the determination of organic species was $<15\%$ (Kawamura and Yasui, 2005; Mochida et al., 2007). Levels of field blanks were within 15% of actual samples, except for phthalic acid (up to 30%). The data reported here were all corrected against the blanks.

3 Results and discussion

3.1 Molecular compositions of dicarboxylic acids, ketoacids and α -dicarbonyls

Average concentrations of OC, EC, and WSOC were 7.2 ± 4.8 , 5.6 ± 5.6 , and $2.1 \pm 1.8 \mu\text{gC m}^{-3}$, respectively. The OC to EC ratio has been used to infer the origin of carbonaceous particles. The average OC/EC ratios at PU site (roadside) were

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lower than those found at the urban/rural sites. The low OC/EC ratio at PU was primarily due to the high EC emissions from automobiles. Higher OC/EC ratios at the rural sites suggest that the transportation of older aerosol as well as SOA were significant. The ratio of WSOC to OC ranged from 0.04 to 0.64, with an average of 0.29 ± 0.16 . The total quantified water-soluble organic compounds (diacids + ketoacids + α -dicarbonyls) (TQWOC) (carbon) accounted for $3.4 \pm 2.2\%$ of OC and $14.3 \pm 10.3\%$ of WSOC.

Concentrations of dicarboxylic acids (C_2 – C_{12}) (including straight-chain saturated, unsaturated, branched-chain, and hydroxylated), ketocarboxylic acids (C_2 – C_9), and α -dicarbonyls in the $PM_{2.5}$ samples are listed in Table 1. In general, large variations of these species were observed among the four sampling cities in PRD. The concentrations of total dicarboxylic acids ranged from 99 to 1340 $ng\ m^{-3}$, with an average of $438 \pm 267\ ng\ m^{-3}$ in PRD. Oxalic acid (C_2) was the most abundant dicarboxylic acid, followed by phthalic acid (Ph). These two species accounted for on average 60% of total quantified water-soluble organic compounds (TQWOC). The concentrations of oxalic acid ranged from 31 to 1035 $ng\ m^{-3}$, which are within the range of the values we reported in the same sampling sites in Hong Kong (Ho et al., 2007). Three phthalic acids including o-, m- and p-isomers were detected. The isomer distribution was characterized by a predominance of phthalic acid followed by terephthalic acid and isophthalic acid, being consistent with those reported in the aerosols in Mt. Tai, China (Fu et al., 2008) and East China Sea (Simoneit et al., 2004). The average concentration of phthalic acid in PRD ($81\ ng\ m^{-3}$) is ~ 2 times higher than that observed in urban area of Tokyo in summer ($29\ ng\ m^{-3}$ on average) (Kawamura and Yasui, 2005), but is close to those reported in the Chinese cities (Ho et al., 2007). Phthalic acid can be formed by photo-degradation of naphthalene (NAP) and other polycyclic aromatic hydrocarbons (PAHs) in atmospheric aerosols (Bunce et al., 1997; Jang and McDow, 1997). NAP is a ubiquitous pollutant in the atmosphere. The concentrations of NAP in urban areas such as Hong Kong have been reported to be as high as $3.5\ \mu g\ m^{-3}$ (Lee et al., 2001). The products generated in the reaction of gas phase NAP with OH radical have lower vapor pressures than NAP, thus promoting the formation of secondary

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organic aerosols (SOA). Besides C₂–C₄ dicarboxylic acids, the concentrations of azelaic acid (C₉) were the highest among the straight-chain saturated carboxylic acids in the PRD. Azelaic acid is an oxidation product of unsaturated fatty acids (Kawamura and Gagosian, 1987). An average abundance of azelaic acid was found to be 13.8 ng m⁻³ in PRD, indicating that aerosols of biological origins are exposed to significant atmospheric processing.

The total concentrations of ketocarboxylic acids ranged from 0.6 to 207 ng m⁻³ (43 ± 48 ng m⁻³ on average). Glyoxylic acid (ωC₂) is the dominant ketocarboxylic acids, followed by pyruvic acid (Pyr) and 4-oxobutanoic acid (ωC₄). Their concentrations are close to those reported in Tokyo, Japan (Kawamura and Yasui, 2005) and other urban sites in China (Ho et al., 2007, 2010). The total concentrations of α-dicarbonyls, including glyoxal and methylglyoxal, ranged from 0.2 to 89 ng m⁻³, with an average of 11 ± 18 ng m⁻³ in PRD. Their concentrations were consistent to those reported in Hong Kong (Li and Yu, 2005) which did not exceed 100 ng m⁻³. α-dicarbonyls have been demonstrated to be precursors to the formation of SOA via heterogeneous processes (Kroll et al., 2005; Liggio et al., 2005). Photo-oxidation of glyoxal can lead the formation of oxalic acid. The higher concentrations of glyoxal and methylglyoxal may represent the greater potential of subsequent SOA formation processing in PRD.

3.2 Molecular compositions of fatty acids and benzoic acid

Concentrations of a homologous series of straight chain saturated fatty acids (C_{12:0}–C_{25:0}), unsaturated acid (oleic C_{18:1}) and benzoic acid are shown in Table 1 as well. The total quantified fatty acids concentrations ranged from below MDL (spell out) to 103 ng m⁻³, with an average of 43.4 ± 27.3 ng m⁻³. Hexadecanoic acid (C_{16:0}), octadecanoic acid (C_{18:0}) and oleic acid (C_{18:1}) are the three most abundant fatty acids in PRD. This was consistent to the data reported by Zheng et al. (2000). The odd number fatty acids with C_{≥19} were below MDL in the sites, demonstrating a strong even to odd predominance for fatty acids. Both biogenic and anthropogenic sources are the essential inputs of fatty acids. Microbial activity is one of important biogenic sources

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(Simoneit and Mazurek, 1982). For anthropogenic sources, $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$ are predominantly emitted from the meat cooking while $C_{16:0}$ can also be directly formed in fossil fuel combustion (Rogge et al., 1991; Schauer et al., 1999, 2002; Zhao et al., 2007a, b). The high concentration of total fatty acids suggests that both cooking and vehicular emissions are important pollution sources in PRD as well as vegetations.

Molecular distributions of fatty acids are characterized by a strong even carbon number predominance with a maximum (C_{max}) at hexadecanoic acid ($C_{16:0}$). Similar distribution patterns of fatty acids have been reported in other urban and rural areas in Hong Kong and China (Zheng et al., 2000; Hou et al., 2006; Fu et al., 2008).

The dominance of even carbon number fatty acid to odd carbon number fatty acid isomers is quantified by Carbon Preference Index (CPI) and is calculated as:

$$CPI_{\text{fatty acid}} = \frac{\sum \text{Even carbon number fatty acids}}{\sum \text{Odd carbon number fatty acids}} \quad (1)$$

The predominance of even carbon numbered fatty acids represents that a significant influence from biological sources of aerosols such as microbial activities and epicuticular waxes of vascular plant (Simoneit and Mazurek, 1982; Simoneit, 1984). Here the CPI was calculated with homologous series of fatty acids ($C_{12:0}$ to $C_{25:0}$). The CPI values of the fatty acids are 19.4, 13.8, 40.4 and 3.26, in GZ, ZQ, PU and HT, respectively. The CPI values are higher in summer than in winter indicate that biogenic source has a larger contribution in hot weather.

Octadecenoic acid (oleic acid, $C_{18:1}$) was detected in most of the urban samples which had concentrations ranged from below MDL to 26 ng m^{-3} ($4.1 \pm 4.7 \text{ ng m}^{-3}$ on average) in PRD. Automobile engine exhaust is one of the pollution sources for $C_{18:1}$ (Rogge et al., 1993b). Ratio of $C_{18:1}$ to $C_{18:0}$ can be used as an indicator for aerosol aging. A lower ratio was observed in aged aerosol as unsaturated fatty acids can be photo-chemically degraded, while saturated fatty acids are more stable in the atmosphere (Kawamura and Gagosian, 1987; Wang et al., 2006). In PRD, an average of $C_{18:1}/C_{18:0}$ ratio was 0.53 ± 0.39 , suggesting an enhanced photochemical degradation of unsaturated fatty acid.

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Benzoic acid was detected in most of the samples in PRD, with an average concentration of $165 \pm 48 \text{ ng m}^{-3}$. Benzoic acid was proposed to be a primary pollutant in the motor vehicles exhaust (Kawamura et al., 1985; Rogge et al., 1993b), and a secondary product from photochemical degradation of aromatic hydrocarbons such as toluene emitted by automobiles (Suh et al., 2003). Guo et al. (2004) found that high daily concentration of toluene, with a maximum of $53 \mu\text{g m}^{-3}$, was determined in Hong Kong. This suggests that major portion of benzoic acid in the PRD aerosols is probably produced by the oxidation of toluene in the atmosphere.

3.3 Summer/winter variations and spatial distribution

Summer/winter variations of the pollutants were found in the four sampling sites. TQ-WOC concentrations ranged from 145 to 1340 ng m^{-3} (544 ng m^{-3} on average) in winter and from 99 to 665 ng m^{-3} (318 ng m^{-3} on average) in summer. These values are similar to those ($90\text{--}1370 \text{ ng m}^{-3}$, 480 ng m^{-3} on average) reported in urban Tokyo (Kawamura and Ikushima, 1993), but are lower to those reported in other urban cities in China (Ho et al., 2007). Total ketocarboxylic acid concentrations ranged from 4.5 to 178 ng m^{-3} (43.9 ng m^{-3} on average) in winter and from 0.59 to 207 ng m^{-3} (42.3 ng m^{-3} on average) in summer, while total dicarbonyl concentrations ranged from 1.3 to 88.6 ng m^{-3} (11.0 ng m^{-3} on average) in winter and from 0.15 to 68.2 ng m^{-3} (11.6 ng m^{-3} on average) in summer. These concentrations are similar to those reported (ketocarboxylic acids = 53 ng m^{-3} ; dicarbonyls = 12 ng m^{-3}) at the Gosan site on Jeju Island, South Korea (Kawamura et al., 2004). Total quantified fatty acids ranged from 2.9 to 103 ng m^{-3} (45.3 ng m^{-3} on average) in winter and from below MDL to 96.1 ng m^{-3} (41.3 ng m^{-3} on average) in summer, while benzoic acid concentrations ranged from 101 to 256 ng m^{-3} (157 ng m^{-3} on average) in winter and from 83.9 to 306 ng m^{-3} (175 ng m^{-3} on average) in summer.

In order to investigate the transport and the source region of air pollutants, 2-day air mass back trajectory analyses were conducted using NOAA HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, NOAA/ARL) with a starting elevation

of 100 m. In winter, prevailing northeasterly wind travels across South China before reaching Hong Kong (Fig. 2a). Total dicarboxylic acids were the most abundant in downwind location of Hong Kong (i.e., PU and HT sites). Air quality in Hong Kong is poorest in winter due to the influence of local sources and polluted air mass transported from South China. In contrast, the highest dicarboxylic concentration was found in the downwind locations in GZ and ZQ during summer, when prevailing southwesterly wind brings warm and damp air masses from the South China Sea through Hong Kong to PRD region (Fig. 2b).

Comparisons of winter and summer concentrations for both individual quantified compounds are shown in Table 1. The highest average concentrations of the TQ-WOC and total quantified fatty acids were found at PU in winter, which is attributable to the mixed contribution of local and regional sources. The concentrations of the organic pollutants in winter were generally higher in PU and HT than in GZ and ZQ. The high abundances of organic aerosols in downwind locations (PU and HT) are due to the emissions from urban local sources and regional long-range transport from PRD when the air mass came from the north. Reversibly, lower concentrations of the TQ-WOC were found at PU and HT in summer because of the upwind locations. The local emission sources were diluted by marine air masses transported from the South China Sea. In contrast, the concentrations of the TQWOC at downwind locations (GZ and ZQ) were 2–3 times higher than those in Hong Kong during summer. Concentrations of total quantified fatty acids at urban sites (GZ, ZQ and PU) were found to be 3–23 times higher than those at background site (HT).

TQWOC were normalized by OC to better discuss summer/winter variations. The relative abundances of TQWOC in OC were higher in summer (1.8–12.4%, 5.4% on average) than in winter (winter: 1.1–5.7, 2.6% on average) except PU site, being consistent with enhanced secondary production of dicarboxylic acids under warmer weather conditions. Abundances of total WSOC in TOC were also higher in summer (20.5% on average) than those in winter (8.1% on average).

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3.4 Correlation analysis and the ratios of selected species

Low molecular weight dicarboxylic acids are mainly produced in the atmosphere by photochemical chain reactions of unsaturated hydrocarbons or fatty acids as well as their oxidation products (Kawamura and Sakaguchi, 1999; Kawamura et al., 1996b); however, their formation mechanisms have been poorly understood. Other than primary emissions, photochemical reactions in the atmosphere play an important role in the formation of dicarboxylic acids. Therefore, the correlation coefficients of selected species were examined in different sites in both seasons. Table 2 shows the correlation coefficients of selected dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls. Strong correlations were observed for C_2 , C_3 , C_4 , C_9 , ωC_2 and ωC_9 in downwind locations, that is, GZ and ZQ in summer and HK and HT in winter, respectively. Other than direct vehicular emission, photochemical processes control the atmospheric concentrations of these species. For instance, ωC_2 , the most abundant ketocarboxylic acid, can be further oxidized to C_2 dicarboxylic acid; thus a good correlation was found between ωC_2 and C_2 ($r = 0.93$ in GZ; $r = 0.98$ in ZQ in summer; and $r = 0.42$ in HK; $r = 0.89$ in HT in winter).

Furthermore, positive correlations of ωC_2 with Gly ($r = 0.85 - 0.99$) are observed in the downwind sites. This is consistent with the atmospheric oxidation process proposed for Gly to ωC_2 (Kawamura et al., 1996c). Malonic (C_3) and succinic (C_4) acids can be oxidized to C_2 via the breakdown of intermediates such as ketomalonic acid (kC_3) (Kawamura and Ikushima, 1993), thus strong correlations were observed among C_2 , C_3 and C_4 in this study. Other acids such as fumaric (F), maleic (M) and methylmaleic (mM) acids are fairly correlated each other ($r = 0.61 - 0.70$). These three dicarboxylic acids are known to be the photooxidation products of toluene, benzene, and xylene. Maleic acid (M) can isomerize to *trans*-fumaric acid (F) by photochemical transformations (Kawamura and Ikushima, 1993). C_2 , sometimes regarded as secondary organic aerosol tracer, has good correlation with sulfate ($r = 0.66$), which is consistent with previous studies. Yu et al. (2005) argue that in-cloud processing has been established to be the dominant formation pathway for oxalate.

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Kawamura and Ikushima (1993) suggested that ratio of C_3 to C_4 can be used as an indicator of enhanced photochemical production of dicarboxylic acids. It is known that C_4 can serve as a precursor of C_3 . In this study, C_3/C_4 ratios ranged between 0.24 and 5.42 with an average of 1.29, which are higher than those reported from vehicular emissions (0.3–0.5) (Kawamura and Kaplan, 1987), and for aerosols in Northern China in summer (0.61) and winter (1.12) (Ho et al., 2007). Our findings also suggest that in addition to primary exhaust, secondary formation of particulate dicarboxylic acids by photo-oxidation reaction is also important in PRD.

The $(F + M + mM)/EC$ ratios at the downwind sampling locations were much higher than those at the upwind sampling sites. The elevated abundance of M, F and mM in aged aerosols indicates that the photooxidation of aromatic compounds to F, M, and mM is important during long-range transport. Good correlations ($r = 0.69$ in downwind sites; $r = 0.85$ in upwind sites) were observed between the TQWOC and WSOC (Fig. 3). These results suggest that dicarboxylic acids, ketocarboxylic acids and dicarbonyls are the major water-soluble organic species in PRD, which are linked to the photochemical chain reactions. The TQWOC contributed more than 15% of WSOC in downwind sites (except HT), suggesting that the water-soluble organic species are one of the major contributors of WSOC in PRD. It is reasonable because there is a sufficient duration for the precursors to form SOC during the long-distance transport to the downwind sampling locations.

4 Summary and conclusions

Molecular compositions of low molecular weight dicarboxylic acids (C_2 – C_{12}), ketocarboxylic acids (ωC_2 – ωC_9 , pyruvic acid), α -dicarbonyls (C_2 – C_3), fatty acids (C_{12} – C_{25}) and benzoic acid were studied in $PM_{2.5}$ samples collected from four sampling locations in PRD during the winter and summer to better understand their spatial and seasonal variations of water-soluble organic species. Oxalic (C_2) acid was found as the most abundant diacid, followed by phthalic acid (Ph) which are similar to other urban cities in China (Ho et al., 2007). The total quantified water-soluble compounds (TQWOC)

(organic carbon) contributed a significant fraction in WSOC ($14.3 \pm 10.3\%$). The average concentration of total quantified fatty acids was $43.4 \pm 27.3 \text{ ng m}^{-3}$. They are derived from both biogenic and anthropogenic sources. The strong even carbon number predominance in fatty acid distributions represents significant influences from biological sources such as microbial activities and epicuticular waxes of vascular plant in PRD region. Octadecenoic acid (oleic acid, $\text{C}_{18:1}$) was detected in most of the urban samples with concentrations ranging from below MDL to 26 ng m^{-3} ($4.1 \pm 4.7 \text{ ng m}^{-3}$ on average) in PRD. Automobile engine exhaust may be one of the pollution sources for $\text{C}_{18:1}$.

The concentrations of the organic pollutants in winter were generally higher in PU and HT than in GZ and ZQ. The high abundances of organic aerosols in downwind locations (PU and HT) are due to the emissions from urban local sources and long-range transport from PRD when the air mass came from the north. In contrast, lower concentrations of the TQWOC were found at the upwind locations of PU and HT in summer.

The local emission sources were diluted by marine air masses transported from South China Sea. These spatial and seasonal variations are consistent with photochemical production and the subsequent accumulation under different meteorological conditions.

Relatively high C_3/C_4 ratios (0.24–5.42 with an average of 1.29) were found for the molecular distributions of dicarboxylic acids in this study, further suggesting that in addition to primary emissions from vehicular emissions, secondary formation of particulate dicarboxylic acids via photo-oxidation reaction is important in PRD. Good correlations ($r = 0.69$ in downwind sites; $r = 0.85$ in upwind sites) were observed between the TQWOC and WSOC, suggesting that dicarboxylic acids, ketocarboxylic acids and dicarbonyls are the major water-soluble organic species in PRD. The TQWOC contributed more than 15% of WSOC in downwind sites (except HT), suggesting that the water-soluble organic species are one of the major contributors of WSOC in PRD.

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formation in China (KZCX2-YW-BR-10)] of the Chinese Academy of Sciences and the Research Grants Council of Hong Kong (PolyU5197/05E). This study was also supported by a Grant-in-Aid No. 19204055 from the Japan Society for the Promotion of Science (JSPS), and the Environment Research and Technology Development Fund (B-0903) of the Ministry of the Environment, Japan.

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Table 1. Concentrations of dicarboxylic acids, ketocarboxylic acids, benzoic acid, and fatty acids in PM_{2.5} samples in PRD during winter and summer in 2006–2007, Guangzhou (GZ), Zhaoqing (ZQ), The Hong Kong Polytechnic University (PU), Hok Tsui (HT).

Compounds (ng m ⁻³)	GZ		ZQ		PU		HT	
	Winter (n = 8)	Summer (n = 7)	Winter (n = 8)	Summer (n = 7)	Winter (n = 8)	Summer (n = 7)	Winter (n = 8)	Summer (n = 7)
Dicarboxylic acids								
Oxalic, C2	182 ± 106	216 ± 97.2	309 ± 159	212 ± 96.9	464 ± 249	92.3 ± 50.4	470 ± 301	77.7 ± 62.2
Malonic, C3	13.3 ± 9.55	18.5 ± 8.79	20.3 ± 15.1	11.4 ± 7.20	26.5 ± 19.7	5.92 ± 5.23	21.0 ± 15.5	10.5 ± 14.7
Succinic, C4	18.4 ± 11.5	11.2 ± 4.24	27.9 ± 17.7	11.5 ± 5.84	23.2 ± 18.0	4.32 ± 1.81	25.4 ± 21.4	3.96 ± 5.76
Glutaric, C5	5.82 ± 3.00	4.72 ± 1.84	8.05 ± 4.15	3.94 ± 1.55	6.64 ± 4.95	1.75 ± 0.50	7.10 ± 4.76	1.24 ± 2.40
Adipic, C6	5.39 ± 2.92	4.85 ± 1.97	7.69 ± 3.96	6.25 ± 2.26	7.00 ± 3.55	2.38 ± 0.89	3.97 ± 2.78	0.48 ± 1.27
Pimeric, C7	2.68 ± 1.91	1.61 ± 1.10	4.29 ± 2.38	2.34 ± 0.95	2.99 ± 2.12	0.94 ± 0.44	2.39 ± 1.77	0.12 ± 0.31
Suberic, C8	0.29 ± 0.18	0.24 ± 0.15	0.60 ± 0.33	0.47 ± 0.32	0.31 ± 0.28	0.02 ± 0.04	0.04 ± 0.07	0.00 ± 0.00
Azelaic, C9	16.3 ± 6.88	14.7 ± 5.52	16.2 ± 6.44	18.4 ± 9.62	24.3 ± 9.94	9.76 ± 3.99	8.40 ± 4.10	1.34 ± 1.34
Sebacic, C10	1.43 ± 0.87	0.94 ± 0.27	1.97 ± 1.15	1.41 ± 0.83	1.90 ± 0.66	0.66 ± 0.23	1.42 ± 0.95	0.00 ± 0.00
Undecanedioic, C11	0.47 ± 0.49	0.00 ± 0.00	0.87 ± 0.50	0.04 ± 0.09	0.09 ± 0.26	0.04 ± 0.10	0.80 ± 0.52	0.00 ± 0.00
Dodecanedioic, C12	0.20 ± 0.27	0.14 ± 0.14	0.13 ± 0.23	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.13 ± 0.19	0.00 ± 0.00
Methylmalonic, iC4	0.19 ± 0.36	0.10 ± 0.10	0.60 ± 0.70	0.02 ± 0.05	0.25 ± 0.28	0.00 ± 0.00	0.30 ± 0.45	0.09 ± 0.24
Methylsuccinic, iC5	1.96 ± 1.10	0.86 ± 0.59	3.71 ± 1.93	3.09 ± 1.11	2.92 ± 2.63	0.00 ± 0.00	2.57 ± 2.16	0.26 ± 0.68
2-Methylglutaric, iC6	0.88 ± 0.46	0.69 ± 0.40	1.65 ± 0.70	0.93 ± 0.42	1.08 ± 0.43	0.19 ± 0.14	0.94 ± 0.65	0.06 ± 0.15
Maleic, M	1.12 ± 0.48	1.41 ± 0.81	1.98 ± 0.69	2.08 ± 2.28	1.52 ± 1.88	0.74 ± 0.43	1.52 ± 1.41	0.12 ± 0.28
Fumaric, F	0.80 ± 0.32	1.75 ± 1.79	0.97 ± 0.68	1.19 ± 0.75	1.20 ± 0.88	0.55 ± 0.20	0.73 ± 0.60	0.18 ± 0.49
Methylmaleic, mM	1.95 ± 1.28	6.21 ± 4.55	8.48 ± 0.97	28.3 ± 9.56	14.0 ± 14.4	2.83 ± 2.00	1.19 ± 1.11	0.07 ± 0.20
Phthalic, Ph	91.8 ± 38.9	215 ± 86.1	36.0 ± 15.3	37.2 ± 21.2	34.1 ± 11.4	32.8 ± 8.50	79.7 ± 54.1	130 ± 75.0
Isophthalic, iPh	3.13 ± 2.01	2.06 ± 0.71	4.47 ± 2.21	2.94 ± 1.40	5.56 ± 1.96	2.77 ± 0.73	1.07 ± 1.09	0.11 ± 0.28
Terephthalic, tPh	31.8 ± 30.9	19.1 ± 8.07	22.7 ± 15.4	10.7 ± 4.85	19.9 ± 9.32	2.54 ± 0.85	19.9 ± 14.4	1.68 ± 2.62
Malic, hC4	0.40 ± 0.37	0.13 ± 0.14	0.23 ± 0.10	0.34 ± 0.11	0.21 ± 0.14	0.00 ± 0.00	0.04 ± 0.12	0.00 ± 0.00
Ketomalonic, kC3	1.86 ± 1.58	1.28 ± 0.84	9.54 ± 8.44	4.43 ± 1.79	4.44 ± 2.79	0.10 ± 0.28	4.09 ± 3.18	0.13 ± 0.34
4-Ketopimelic, kC7	1.73 ± 1.04	1.56 ± 0.99	3.47 ± 2.78	1.55 ± 0.91	2.39 ± 1.42	0.30 ± 0.28	2.99 ± 2.19	0.32 ± 0.59
Total	384 ± 171	523 ± 134	490 ± 241	361 ± 156	644 ± 327	161 ± 58.6	656 ± 346	228 ± 72.7
Ketocarboxylic acids								
Pyruvic	4.68 ± 2.12	2.64 ± 1.63	10.4 ± 12.4	35.2 ± 11.4	21.1 ± 18.8	1.56 ± 1.05	4.94 ± 2.87	2.96 ± 4.62
Glyoxylic, ωC2	13.0 ± 6.70	11.0 ± 5.46	25.4 ± 14.4	62.8 ± 20.9	38.5 ± 37.1	1.16 ± 1.01	13.5 ± 7.49	7.82 ± 11.7
3-Oxopropanoic, ωC3	0.51 ± 0.31	0.19 ± 0.07	0.64 ± 0.43	0.01 ± 0.02	0.28 ± 0.13	0.00 ± 0.00	0.12 ± 0.09	0.04 ± 0.11
4-Oxobutanoic, ωC4	4.63 ± 3.61	2.31 ± 1.54	7.62 ± 3.83	29.5 ± 10.2	14.4 ± 13.9	0.70 ± 0.26	5.91 ± 3.95	0.79 ± 0.88
9-Oxononanoic, ωC9	1.91 ± 1.52	3.34 ± 1.64	1.93 ± 1.42	4.31 ± 2.86	3.92 ± 2.58	1.96 ± 0.78	2.12 ± 1.60	0.76 ± 1.62
Total	24.7 ± 12.0	19.5 ± 9.59	45.9 ± 26.3	132 ± 40.4	78.2 ± 63.7	5.38 ± 2.17	26.6 ± 15.5	12.4 ± 13.5

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Table 1. Continued.

Compounds (ng m ⁻³)	GZ		ZQ		PU		HT	
	Winter (n = 8)	Summer (n = 7)	Winter (n = 8)	Summer (n = 7)	Winter (n = 8)	Summer (n = 7)	Winter (n = 8)	Summer (n = 7)
<i>α</i> -dicarbonyls								
Glyoxal, Gly	3.86 ± 1.78	1.96 ± 1.07	6.00 ± 2.19	13.0 ± 4.33	7.23 ± 6.56	1.19 ± 0.30	2.36 ± 1.35	0.47 ± 0.70
Methylglyoxal, MeGly	1.37 ± 1.70	3.15 ± 1.31	3.45 ± 1.66	25.2 ± 10.8	17.9 ± 26.4	0.43 ± 0.28	1.61 ± 1.32	0.92 ± 0.80
Total	5.23 ± 3.27	5.11 ± 2.13	9.45 ± 3.76	38.2 ± 15.1	25.2 ± 32.8	1.62 ± 0.45	3.97 ± 2.46	1.38 ± 1.36
Sum of total quantified water-soluble organic	414 ± 184	547 ± 144	546 ± 268	531 ± 208	748 ± 381	168 ± 60.3	687 ± 361	241 ± 77.9
Benzoic acid	159 ± 45.6	215 ± 34.5	155 ± 39.8	156 ± 74.2	154 ± 40.7	128 ± 9.18	159 ± 42.0	201 ± 31.6
Fatty acids								
Tridecanoic acid, C _{13:0}	2.60 ± 1.28	1.95 ± 1.59	4.74 ± 2.27	4.03 ± 2.81	3.29 ± 1.91	0.51 ± 0.32	3.11 ± 1.96	0.39 ± 0.84
Tetradecanoic acid, C _{14:0}	7.21 ± 2.97	4.80 ± 0.74	12.0 ± 6.58	8.35 ± 2.68	5.78 ± 2.56	1.73 ± 0.69	2.79 ± 1.84	0.09 ± 0.23
Hexadecanoic acid, C _{16:0}	24.0 ± 14.5	28.2 ± 7.96	16.5 ± 5.42	28.2 ± 9.49	23.8 ± 8.96	18.9 ± 5.79	3.30 ± 3.76	0.66 ± 0.81
Heptadecanoic acid, C _{17:0}	0.48 ± 0.34	0.50 ± 0.22	0.51 ± 0.68	0.56 ± 0.42	0.26 ± 0.53	0.14 ± 0.15	0.32 ± 0.43	0.00 ± 0.00
Octadecanoic acid, C _{18:0}	7.95 ± 3.91	9.07 ± 3.51	7.87 ± 2.73	17.5 ± 6.80	12.6 ± 5.70	8.49 ± 2.64	1.73 ± 2.37	1.44 ± 1.41
Octadecenoic acid, C _{18:1}	5.89 ± 8.32	3.34 ± 1.92	3.23 ± 1.25	9.24 ± 2.25	6.46 ± 4.99	4.99 ± 3.05	0.17 ± 0.49	0.00 ± 0.00
Eicosanoic acid, C _{20:0}	1.20 ± 0.41	1.00 ± 0.24	1.24 ± 0.26	1.25 ± 0.35	1.81 ± 0.68	1.00 ± 0.55	1.03 ± 1.06	0.00 ± 0.00
Docosanoic acid, C _{22:0}	2.05 ± 0.74	1.47 ± 0.27	2.43 ± 0.78	1.40 ± 0.46	3.47 ± 1.66	1.87 ± 0.41	1.99 ± 1.23	0.26 ± 0.33
Tetracosanoic acid, C _{24:0}	2.05 ± 0.76	1.25 ± 0.22	2.40 ± 1.02	1.36 ± 0.52	2.62 ± 1.68	0.93 ± 0.62	2.51 ± 1.66	0.24 ± 0.30
Sum of fatty acids	53.4 ± 28.9	51.6 ± 13.8	50.9 ± 13.5	71.9 ± 23.7	60.1 ± 22.6	38.6 ± 11.5	17.0 ± 12.8	3.08 ± 3.29
OC (μg m ⁻³)	9.29 ± 5.18	5.40 ± 1.21	9.69 ± 4.75	3.93 ± 0.87	13.9 ± 4.41	5.67 ± 1.87	6.82 ± 3.55	1.84 ± 0.82
EC (μg m ⁻³)	5.12 ± 4.45	2.86 ± 1.66	4.40 ± 2.29	1.76 ± 0.28	14.5 ± 2.13	14.7 ± 4.39	3.03 ± 1.27	0.67 ± 0.23
WSOC (μg m ⁻³)	2.68 ± 1.43	1.47 ± 0.51	4.66 ± 2.52	1.75 ± 1.00	2.53 ± 1.64	0.36 ± 0.05	2.33 ± 1.05	0.36 ± 0.21

Table 2. Correlation coefficients of selected dicarboxylic acids, ketocarboxylic acids and dicarbonyls at four sampling sites in PRD in winter and summer seasons.

GZ winter	C2	C3	C4	C9	kC3	@C2	@C9	Gly	GZ summer	C2	C3	C4	C9	kC3	@C2	@C9	Gly
C2	1.00	0.74	0.77	0.78	0.46	0.82	0.25	0.62									
C2	1.00	0.82	0.95	0.63	0.57	0.93	0.68	0.83									
C3		1.00	0.95	0.74	0.81	0.84	0.00	0.63	C3		1.00	0.91	0.91	0.28	0.97	0.74	0.84
C4			1.00	0.83	0.69	0.92	-0.08	0.77	C4			1.00	0.70	0.56	0.97	0.74	0.92
C9				1.00	0.28	0.98	-0.06	0.92	C9				1.00	0.02	0.85	0.56	0.59
kC3					1.00	0.44	0.05	0.13	kC3					1.00	0.41	0.07	0.63
@C2						1.00	-0.04	0.92	@C2						1.00	0.72	0.85
@C9							1.00	-0.14	@C9							1.00	0.76
Gly								1.00	Gly								1.00
ZQ winter	C2	C3	C4	C9	kC3	@C2	@C9	Gly	ZQ summer	C2	C3	C4	C9	kC3	@C2	@C9	Gly
C2	1.00	0.67	0.84	0.87	0.67	0.97	0.68	0.94	C2	1.00	0.96	0.90	0.77	0.89	0.98	0.70	0.88
C3		1.00	0.47	0.69	0.32	0.65	0.96	0.57	C3		1.00	0.79	0.77	0.80	0.99	0.75	0.92
C4			1.00	0.49	0.94	0.85	0.43	0.88	C4			1.00	0.64	0.80	0.82	0.47	0.62
C9				1.00	0.24	0.79	0.72	0.71	C9				1.00	0.87	0.79	0.94	0.86
kC3					1.00	0.75	0.31	0.83	kC3					1.00	0.87	0.77	0.88
@C2						1.00	0.68	0.99	@C2						1.00	0.74	0.94
@C9							1.00	0.62	@C9							1.00	0.87
Gly								1.00	Gly								1.00
PU winter	C2	C3	C4	C9	kC3	@C2	@C9	Gly	PU summer	C2	C3	C4	C9	kC3	@C2	@C9	Gly
C2	1.00	0.94	0.92	0.80	0.54	0.42	0.56	0.42	C2	1.00	0.98	0.93	0.94	0.92	0.78	-0.02	0.44
C3		1.00	0.98	0.81	0.67	0.41	0.44	0.33	C3		1.00	0.97	0.97	0.90	0.72	-0.03	0.53
C4			1.00	0.74	0.50	0.45	0.37	0.34	C4			1.00	0.92	0.89	0.73	-0.05	0.64
C9				1.00	0.73	0.69	0.85	0.61	C9				1.00	0.88	0.65	0.04	0.46
kC3					1.00	0.18	0.53	0.29	kC3					1.00	0.90	0.08	0.37
@C2						1.00	0.72	0.98	@C2						1.00	0.15	0.40
@C9							1.00	0.73	@C9							1.00	0.35
Gly								1.00	Gly								1.00
HT winter	C2	C3	C4	C9	kC3	@C2	@C9	Gly	HT summer	C2	C3	C4	C9	kC3	@C2	@C9	Gly
C2	1.00	0.84	0.82	0.77	0.60	0.89	0.67	0.71	C2	1.00	0.75	0.95	0.89	0.84	0.22	0.29	0.95
C3		1.00	0.95	0.73	0.66	0.83	0.92	0.76	C3		1.00	0.74	0.61	0.49	0.23	0.15	0.77
C4			1.00	0.63	0.53	0.76	0.91	0.70	C4			1.00	0.98	0.94	0.24	0.27	1.00
C9				1.00	0.96	0.97	0.67	0.97	C9				1.00	0.98	0.23	0.32	0.97
kC3					1.00	0.88	0.62	0.93	kC3					1.00	0.25	0.25	0.93
@C2						1.00	0.75	0.95	@C2						1.00	-0.12	0.24
@C9							1.00	0.77	@C9							1.00	0.25
Gly								1.00	Gly								1.00

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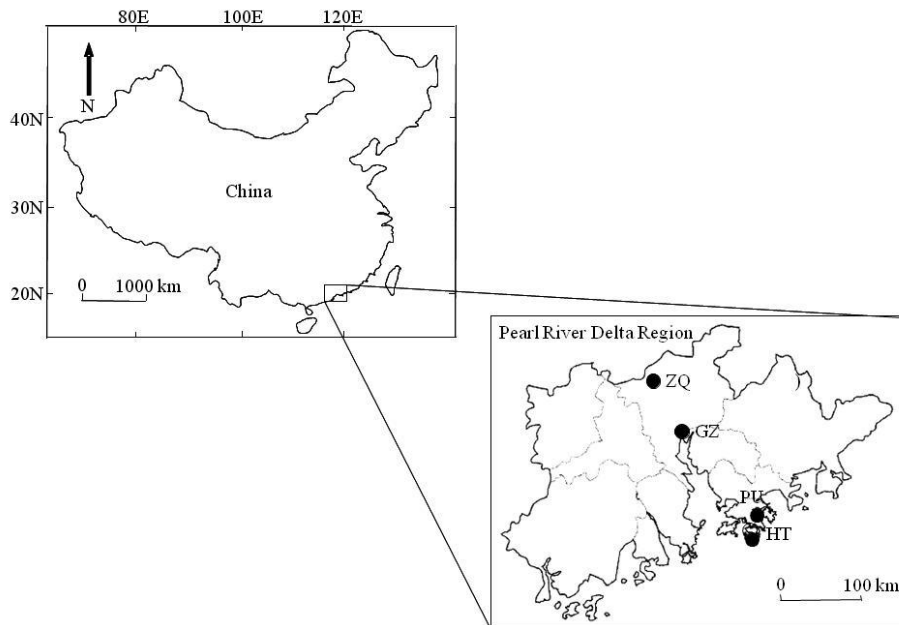


Fig. 1. A map showing sampling sites in this study, Guangzhou (GZ), Zhaoqing (ZQ), The Hong Kong Polytechnic University (PU), Hok Tsui (HT).

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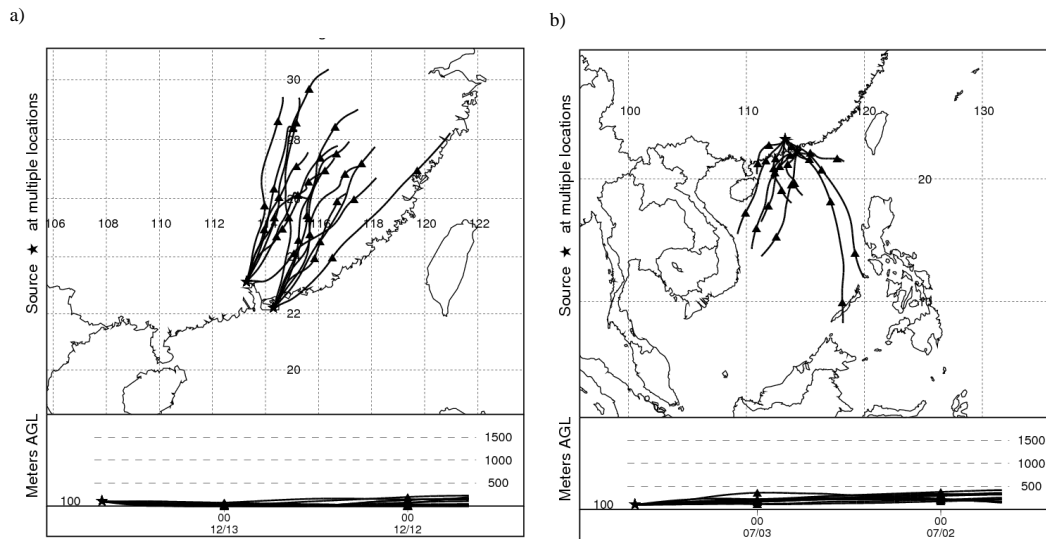


Fig. 2. 2-day air mass back trajectories in summer (a) and in winter (b) during the sampling period.

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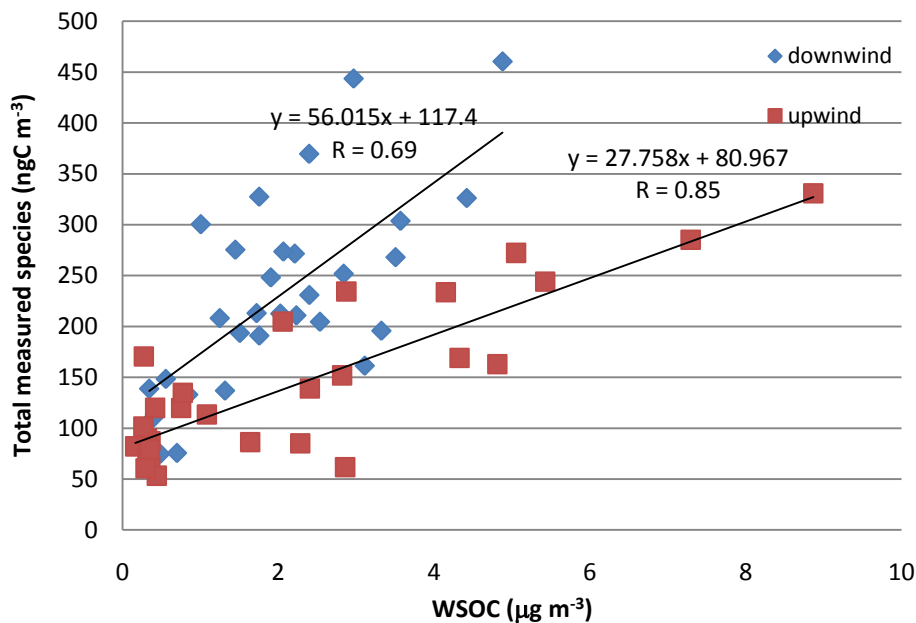


Fig. 3. Relationship between the concentrations of total quantified water-soluble organic compounds and total water-soluble organic carbon (WSOC).

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